CD221. LECTURE 9. IDEAL GAS. LEGENDRE TRANSFORMS

• Entropy Estimates from the Sackur-Tetrode Equation

     To get a feel for some typical entropy values of real gases, let's apply the Sackur-Tetrode equation, viz.,

$$S = \frac{5Nk_B}{2} + Nk_B \ln\left[\left(\frac{4\pi m}{3h^2}\right)^{3/2} \frac{U^{3/2}V}{N^{5/2}}\right] \tag{1}$$

to 1 mole of He at room temperature (300 K) and atmospheric pressure (1.013×10^5 Pa .) For such a gas, the ideal gas law $PV = Nk_BT$ predicts that the volume will be

$$V = \frac{1\times8.314\times300}{1.013\times10^5} \approx 0.025 \text{ m}^3,$$

while the energy equation $U = \frac{3}{2}Nk_BT$ predicts that the energy will be

$$U = \frac{3\times1\times8.314\times300}{2} \approx 3700 \text{ J}$$

If these numbers are substituted into Eq. (1), we find that

$$S \approx 126 \text{ J/K}.$$

It turns out that for many other gases under the same conditions, the calculated entropies are on the order of a few hundreds of Joules per Kelvin. (Energies tend to be on the order of a few kJ per mole.)

• Other Results from the Sackur-Tetrode Equation

(i) Expansion

     Equation (1) shows explicitly how S changes in response to changes in the variables U, V or N. The nature of the dependence of S on V is particularly transparent when U and N are constant. Under these conditions, a change in volume from an initial value V_i to a final value V_f leads to an entropy change ΔS given by

$$\Delta S = Nk_B \ln\left(\frac{V_f}{V_i}\right), \qquad U, N \text{ constant} \tag{2}$$

This relation is applicable to two kinds of processes that have practical relevance: (1) quasi-static isothermal expansion, and (2) free expansion. In the first, a fixed amount of

gas pushes against a piston, doing work, while heat simultaneously enters the system to maintain T constant (and fixing U thereby.) In the second, a fixed amount of the gas expands into an evacuated chamber. If the chamber is closed – meaning its boundary is rigid, adiabatic and impermeable – the expansion is accompanied by no transfer of heat and no performance of work. The entropy increase for both these systems is given by Eq. (2).

(ii) <u>Mixing</u>

Another kind of process can also lead to entropy increase – mixing. Consider a container divided into two chambers, one chamber of volume V_1 having N_1 molecules of a monatomic ideal gas at temperature T and pressure P, and the other chamber of volume V_2 having N_2 molecules of a *different* monatomic gas at the *same* temperature and pressure. The arrangement is as shown below:
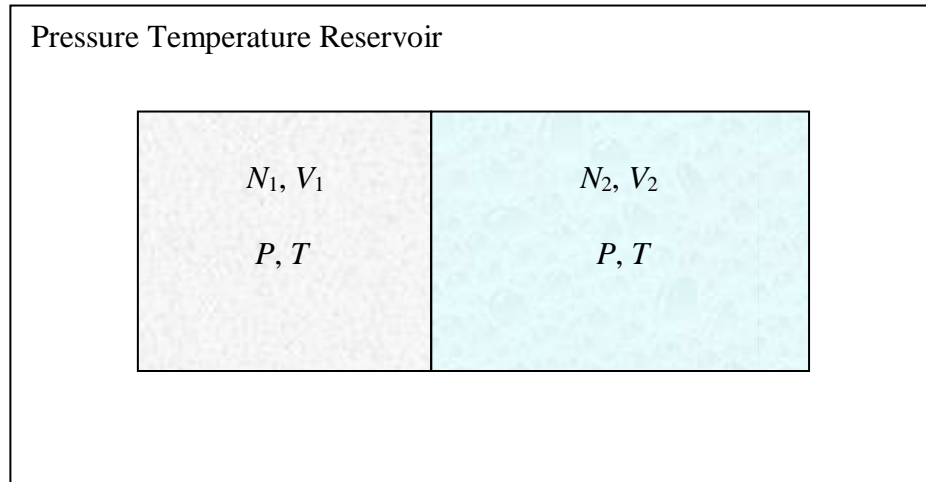
If the partition between the two chambers is now removed, what is the overall change in the entropy?

From the equations for the entropy and energy of an ideal gas, the initial entropy S_{1i} of the gas in chamber 1 is

$$S_{1i} = \frac{5N_1 k_B}{2} + N_1 k_B \ln\left[\left(\frac{4\pi m_1}{3h^2}\right)^{3/2} \left(\frac{3k_B T}{2}\right)^{3/2} \frac{V_1}{N_1}\right]$$

$$= \frac{5N_1 k_B}{2} + N_1 k_B \ln\left(\frac{V_1}{N_1}\right) + C_1 \tag{3}$$

where $C_1 = (3N_1 k_B / 2)\ln(2\pi k_B T m_1 / h^2)$. In the same way, the final entropy S_{1f} of the gas in chamber 1 is

$$S_{1f} = \frac{5N_1k_B}{2} + N_1k_B \ln\left(\frac{V}{N_1}\right) + C_1 \qquad (4)$$

where V is now the total volume of the two chambers, i.e., $V = V_1 + V_2$. Hence, the change in entropy ΔS_1 of this gas is found as

$$\Delta S_1 = S_{1f} - S_{1i} = N_1k_B \ln\left(\frac{V}{V_1}\right) \qquad (5)$$

For the gas in the second chamber, the entropy change ΔS_2 is likewise found as

$$\Delta S_2 = S_{2f} - S_{2i} = N_2k_B \ln\left(\frac{V}{V_2}\right) \qquad (6)$$

Thus the overall entropy change ΔS becomes

$$\Delta S = \Delta S_1 + \Delta S_2 = N_1k_B \ln\left(\frac{V}{V_1}\right) + N_2k_B \ln\left(\frac{V}{V_2}\right) \qquad (7)$$

which is positive (meaning there is an overall increase in the entropy.) If it so happened that initially the two chambers were of equal volume and contained exactly the same number of molecules of each gas (such that $V_1 = V_2 = V/2$ and $N_1 = N_2 = N$), then $\Delta S = Nk_B \ln 2 + Nk_B \ln 2 = 2Nk_B \ln 2$. Thus, the mixing of two different ideal gases at constant P and T is accompanied by an *increase* in the entropy, and this change is called the <u>entropy of mixing</u>.

(iv) <u>The Gibbs Paradox</u>

What if, prior to removal of the internal partition in the mixing experiment above, the gases in the two separate chambers were actually the *same*? Intuitively, there should be no change in the overall entropy because there's no mixing as such – the condition of the system before and after the removal of the partition is macroscopically unchanged. Does statistical mechanics, as embodied in the Sackur-Tetrode equation, reach the same conclusion?

In the initial state, the entropy S_i of the composite system is

$$S_i = \frac{5}{2}(N_1 + N_2)k_B + N_1k_B \ln\left(\frac{V_1}{N_1}\right) + N_2k_B \ln\left(\frac{V_2}{N_2}\right) + C' \qquad (8)$$

where $C' = (N_1 + N_2)k_B \ln(2\pi m_1 k_B T / h^2)^{3/2}$, while in the final state, when $N_1 + N_2$ molecules of the gas occupy a volume $V_1 + V_2$ at temperature T and pressure P, the entropy S_f is

$$S_f = \frac{5}{2}(N_1 + N_2)k_b + (N_1 + N_2)k_B \ln\left(\frac{V_1 + V_2}{N_1 + N_2}\right) + C' \qquad (9)$$

Hence,

$$\Delta S = S_f - S_i = (N_1 + N_2)k_B \ln\left(\frac{V_1 + V_2}{N_1 + N_2}\right) - N_1 k_B \ln\left(\frac{V_1}{N_1}\right) - N_2 k_B \ln\left(\frac{V_2}{N_2}\right)$$

$$= N_1 k_B \ln\left(\frac{V}{V_1}\right) + N_2 k_B \ln\left(\frac{V}{V_2}\right) - N_1 k_B \ln\left(\frac{N}{N_1}\right) - N_2 k_B \ln\left(\frac{N}{N_2}\right) \qquad (10)$$

where $V = V_1 + V_2$ and $N = N_1 + N_2$. Therefore,

$$\Delta S = N_1 k_B \ln\left(\frac{V N_1}{V_1 N}\right) + N_2 k_B \ln\left(\frac{V N_2}{V_2 N}\right) \qquad (11)$$

Now since P and T are fixed, it follows that $PV_1 = N_1 k_B T$, $PV_2 = N_2 k_B T$ and $PV = N k_B T$, and so $V_1 / N_1 = k_B T / P = V_2 / N_2 = V / N$. Substituting these results into Eq. (11), we get $\Delta S = 0$, establishing that the statistical mechanical prediction is indeed consistent with thermodynamic expectation.

The source of this agreement can be traced directly to the factor of $N!$ that was included (by hand) in the expression for the number of microstates of the ideal gas, Ω, with energies between U and $U - dU$. The rationale for its inclusion there was to account for the presumed indistinguishability of real particles. If the factor had been omitted, the expression for the entropy would have been

$$S = \frac{3N k_B}{2} + N k_B \ln\left[\left(\frac{4\pi m}{3h^2}\right)^{3/2} \frac{U^{3/2} V}{N^{3/2}}\right] \qquad (12)$$

and with this expression, the entropy of mixing of two identical ideal monatomic gases at the same temperature and pressure but having N_1 and N_2 molecules and occupying V_1 and V_2 volumes would have been

$$\Delta S = N_1 k_B \ln\left(\frac{V}{V_1}\right) + N_2 k_B \ln\left(\frac{V}{V_2}\right) \qquad (13)$$

a result which is clearly positive, and which is therefore in conflict with bulk thermodynamics. This conflict, originating in the assumption of the *distinguishability* of ideal gas particles is called the <u>Gibbs paradox</u>. As we've seen, the paradox is resolved as soon as the particles are assumed to be indistinguishable (which, in any case, they are required to be by quantum mechanics.)

• <u>Other Approaches to the Solution of the Fundamental Problem of Thermodynamics</u>

Let's pause to take stock of how far we've come. We began these lectures by asking why systems evolve to new states when changes are made in their surroundings, and we've learnt that they do so to maximize a quantity called the entropy, denoted *S*. We've also learnt how to calculate this quantity from a knowledge solely of the properties of the particles that make up the system. This calculation reduces to counting the different ways in which a fixed amount of energy *U* can be distributed among the system's *N* constituent particles when they occupy a volume *V*. The number of such ways, Ω, is a function of the variables *U*, *V* and *N*, and is related to *S* through the Boltzmann equation, $S = k_B \ln \Omega(U,V,N)$, which leads to an equation $S = S(U,V,N)$ that contains all the thermodynamic information about the system. We've further seen that the calculation of Ω (technically called the microcanonical partition function) is fairly easy to carry out for certain systems (the Einstein solid, a 2-D polymer, and the ideal gas) and that the predictions that follow from it are consistent with empirical data.

But if we tried to extend this approach of counting states to more complicated systems, to systems, for example, in which inter-particle interactions were important, we would quickly run into difficulties. These difficulties would be further compound if the system happened to be described, at the macroscopic level, not by *U*, *V* and *N*, but by *T*, *V* and *N*, say, or *T*, *P* and *N*, which is often how it would be described in the laboratory.

So although the present mathematical formalism can provide the answers to any thermodynamic question *in principle*, it is not universally applicable *in practice*. We're therefore motivated to ask the following question: Are there any general principles – analogous to the entropy maximization principle – that would allow us to determine the direction of evolution of macrostates that are defined by one or more *intensive* variables? To address this question, we should recall that the entropy maximization principle is a statement about the values the variables *U*, *V* and *N* must take in order that the function

$$S = S(U,V,N) \tag{14}$$

tends to increase. We've seen that this function can be inverted, such that

$$U = U(S,V,N) \tag{15}$$

Given that Eqs. (14) and (15) are equivalent in terms of their thermodynamic content, should *U*, like *S*, therefore be governed by an extremization principle that determines the state that systems evolve to following the release of an internal constraint? In other

words, as systems equilibrate, do they do so by minimizing or maximizing the energy at some fixed value of the entropy?

What we know at the moment is that

$$\left(\frac{\partial S}{\partial X}\right)_U = 0 \quad \text{and} \quad \left(\frac{\partial^2 S}{\partial X^2}\right)_U < 0 \tag{16}$$

where X stands for some extensive variable (perhaps V or N). It's understood that the partial derivatives in (16) are taken at constant U and at constant value of the other remaining extensive variable, which is not shown to save space.

What we'd now like to know is whether Eq. (16) says anything about $\left(\frac{\partial U}{\partial X}\right)_S$ and $\left(\frac{\partial^2 U}{\partial X^2}\right)_S$. To answer this question, we need to somehow re-express these derivatives in terms of the derivatives in (16). We can use the following identity for this purpose (see Sec. A.4 in Callen):

$$\left(\frac{\partial y}{\partial x}\right)_{\psi,z} = -\frac{\left(\partial \psi / \partial x\right)_{y,z}}{\left(\partial \psi / \partial y\right)_{x,z}} \tag{17}$$

If we apply this result to $(\partial U / \partial X)_S$, we get

$$\left(\frac{\partial U}{\partial X}\right)_S = -\frac{\left(\partial S / \partial X\right)_U}{\left(\partial S / \partial U\right)_X}$$

$$= 0 \quad \text{(at the maximum in } S.) \tag{18}$$

So U is at an extremum when S is at its maximum. Is this extremum a maximum or a minimum? To answer this question we need to know the sign of the second derivative of U with respect to X at constant S. This sign is determined as follows:

First, for convenience define $Y = (\partial U / \partial X)_S$. Then

$$\left(\frac{\partial^2 U}{\partial X^2}\right)_S = \left(\frac{\partial Y}{\partial X}\right)_S \tag{19}$$

Now, in general, away from the entropy maximum, Y is a function of S and X. But S itself is a function of U and X, so we can think of Y as a function of U and X too, which means that

$$dY = \left(\frac{\partial Y}{\partial U}\right)_X dU + \left(\frac{\partial Y}{\partial X}\right)_U dX \qquad (20)$$

If Eq. (20) is divided by the infinitesimal quantity dX at constant S, the result is

$$\left(\frac{\partial Y}{\partial X}\right)_S = \left(\frac{\partial Y}{\partial U}\right)_X Y + \left(\frac{\partial Y}{\partial X}\right)_U$$

$$= \left(\frac{\partial Y}{\partial X}\right)_U \quad \text{(at } S = S_{\text{max}}, \text{ because } Y = 0\text{)}$$

$$= \left(\frac{\partial}{\partial X}\left(\frac{\partial U}{\partial X}\right)_S\right)_U \quad \text{(putting back the definition of } Y) \qquad (21)$$

Use of the identity Eq. (26) again leads to:

$$\left(\frac{\partial Y}{\partial X}\right)_S = \left(\frac{\partial}{\partial X}\frac{-(\partial S/\partial X)_U}{(\partial S/\partial U)_X}\right)_U \qquad (22)$$

On the RHS of Eq. (22), the operation of differentiating with respect to X can be carried out using the product rule, which yields

$$\left(\frac{\partial Y}{\partial X}\right)_S = -\frac{1}{(\partial S/\partial U)_X}\left(\frac{\partial^2 S}{\partial X^2}\right)_U + \left(\frac{\partial S}{\partial X}\right)_U \frac{1}{(\partial S/\partial U)_X^2}\frac{\partial^2 S}{\partial X\partial U}$$

$$= -T\left(\frac{\partial^2 S}{\partial X^2}\right)_U + 0 \quad \text{(at } S = S_{\text{max}} \text{ because } \left(\frac{\partial S}{\partial X}\right)_U = 0\text{)} \qquad (23)$$

And because $\left(\dfrac{\partial^2 S}{\partial X^2}\right)_U < 0$ at $S = S_{\text{max}}$, it follows from Eq. (23) and the definition of Y

that

$$\left(\frac{\partial^2 U}{\partial X^2}\right)_S > 0 \qquad (24)$$

which means that the extremum in U is actually a minimum for a given value of S. So we can now enunciate an *energy minimum principle* analogous to our entropy maximum principle: **The equilibrium value of any unconstrained internal parameter is such as to minimize the energy for a given value of the total entropy.**

However, this energy minimum principle is still expressed in terms of variables – S, V and N – that in a practical sense are also not the most convenient to work with. So it's important that we try and find still other equivalent representations of the current thermodynamic formalisms.


• Expressing fundamental relations in equivalent forms

The specific question we now want to address is the following: given the fundamental equation $U = U(S,V,N)$, is there a function ψ, equivalent to U, that is a function of one or more of the variables T, P and μ, such that the equilibrium value of an unconstrained parameter extremizes ψ? To answer this question, consider first a simpler illustrative example. Let y be some function of a single variable x, i.e., let

$$y = y(x) \tag{25}$$

This equation defines a curve in the x-y plane, such as the one below:
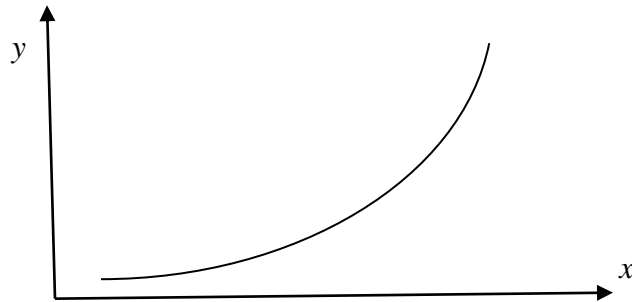
But plotting a series of x values against their corresponding y values isn't the only way to define the locus of this curve. You can also do it by drawing a set of straight lines with just the right slopes and just the right intercepts – the points where one line intersects the next then traces out exactly the same curve. The idea is illustrated below,
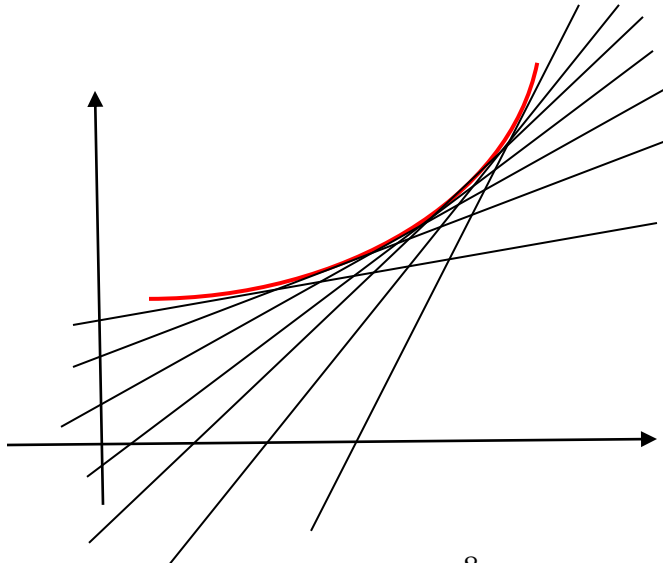
where the red line in this figure marks the trajectory of the points of intersection of successive straight lines. If the slopes of these lines are denoted p and the intercepts ψ, the function

$$\psi = \psi(p) \tag{26}$$

plots these lines out, and thus effectively reconstructs the curve $y = y(x)$ as their *envelope*. In this way, $\psi = \psi(p)$ is entirely equivalent to $y = y(x)$.

The question now is: how to get just the right slopes and just the right intercepts? The method is the following: select some point (x,y) on the given curve and draw a tangent to it, as shown:
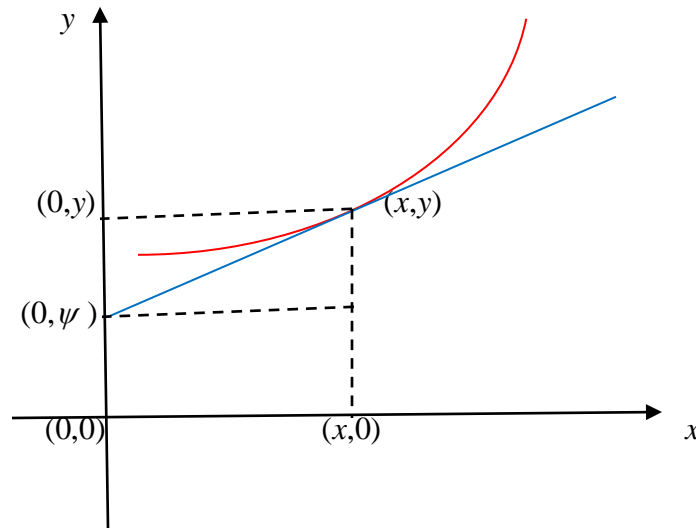
Determine the slope p at the point (x,y) using

$$p = \frac{\text{increase in } y}{\text{increase in } x} = \frac{y - \psi}{x - 0} \tag{27}$$

Rearrange Eq. (27) as

$$\psi = y - px \tag{28}$$

Finally, eliminate y and x from this equation. Do this by first replacing y by its expression in terms of x, and then replacing x by its expression in terms of p (which itself is obtained by inverting $p = dy/dx = p(x)$.) When the dust settles, what we're left with is $\psi = \psi(p)$.

9

In Eq. (28), ψ is said to be the <u>Legendre transform of y with respect to x</u> and is denoted

$$\psi = y[p] \qquad (29)$$

• <u>Generalizations</u>

Suppose y is a function of many variables, such that

$$y = y(x_0, x_1, \cdots, x_t) \qquad (30)$$

By generalizing Eq. (28), we can construct a function ψ equivalent to Eq. (30) that depends on the slopes

$$p_k = \left(\frac{\partial y}{\partial x_k} \right)_{x_i \neq x_k}, \qquad k = 0,1,\cdots,t \qquad (31)$$

as the independent variables instead of the x's. The generalization is

$$\psi = y - \sum_{k=0}^{t} p_k x_k \qquad (32\text{a})$$

$$\equiv y[p_0, p_1, \cdots, p_t] \qquad (32\text{b})$$

and ψ is said to be the Legendre transform of y with respect to $x_0, x_1, \cdots, x_t$; it becomes a function solely of $p_0, p_1, \cdots, p_t$ once y is eliminated from Eq. (32a) using Eq. (30) and the $t+1$ x's are eliminated using the $t+1$ equations of Eq. (31).

Partial Legendre transforms can also be constructed. Suppose, once again, that y is some function of many variables, such that

$$y = y(x_0, x_1, \cdots, x_s, x_{s+1}, \cdots, x_t) \qquad (33)$$

Analogous to Eq. (32a), we can construct a function ψ equivalent to Eq. (33) that depends on the slopes p_k of a *subset* of the x variables in Eq. (33) (such as $x_0, x_1, \cdots, x_s$). For this case, the definition of ψ is

$$\psi = y - \sum_{k=0}^{s} p_k x_k \qquad (34\text{a})$$

$$\equiv y[p_0, p_1, \cdots, p_s] \qquad (34\text{b})$$

where

$$p_k = \left(\frac{\partial y}{\partial x_k}\right)_{x_i \neq x_k}, \qquad k = 0,1,\cdots,s \qquad\qquad (34c)$$

Once y is eliminated from (34a) using Eq. (33) and the $s+1$ x's are eliminated using the $s+1$ equations of Eq. (34c), ψ in Eq. (34a) becomes a function *both* of $p_0, p_1, \cdots, p_s$ *and* of $x_{s+1}, \cdots, x_t$.